ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Data Requirement: EPA Guideline: Non-guideline, 835.6100, 835.6200
OECD Data Point: IIA 4.9 Other/special studies

Test material:
Common names: Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin
Chemical name: Refer to the Attachment II
IUPAC: Refer to the Attachment II

José Luis Meléndez 10/24/2011

Primary Reviewer: José L. Meléndez, Chemist

Secondary Reviewer: Reuben Baris, Environmental Scientist
EFED's Pyrethroid Review Team Representative

ANALYTICAL METHOD: Willoh, J.M., 2010, "Validation of the Residue Analytical Methods: 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin and Permethrin in Wastewater Treatment Primary Sludge,' Dated October 21, 2010 and 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin and Permethrin in Wastewater Treatment Dewatered Cake,' Dated October 20, 2010." Laboratory Validation of Morse Laboratories, LLC Analytical Methods Meth-204 and Meth-205. Morse Labs Project No.: ML10-1641-HQI. Date of the Report February 3, 2011. Performed by Morse Laboratories, LLC, and Submitted by Pyrethroid Working Group, 219 pp. (MRID 48638601)

INDEPENDENT LABORATORY VALIDATION: Not Available

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

EXECUTIVE SUMMARY

The method is designed for the quantitative determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in primary sludge and dewatered cake samples (*i.e.*, biosolids) from Publicly Owned Treatment Works (POTWs). The method was created by Morse Laboratories, LLC. The Agency found that this method does not meet the criteria for a scientifically valid method and only provides limited information for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in primary sludge and dewatered cake samples. The major problem of the method is that it does not have a true independent laboratory validation. LODs and LOQs are highly uncertain because only two matrix blank samples were tested for each analyte.

Method Summary: Samples were taken from a POTW facility in Suffern, NY, a secondary treatment facility. Primary sludge samples were collected from the primary settling tanks and they are a combination of primary settled solids after pretreatment (grit removal, bar screens), and waste solids after activated sludge biological treatment (proportions of each were not provided). Dewatered cake samples were collected as digested sludge from the anaerobic digesters, after being dewatered using centrifuge. The sample residues are extracted by shaking with a methanol-water mixture and partitioning the mixture with hexane. After centrifuging, an aliquot of the hexane layer is subjected to a silica solid phase extraction (SPE) cleanup procedure. The residue is determined by gas chromatography with mass selective detection using negative chemical ionization (GC-MSD/NCI). Based upon the study, uncertain estimates of the LODs and LOQs were obtained because data were available for only two matrix blank samples.

For individual (*i.e.*, chemical by chemical) LODs and LOQs, refer to Attachment I (Checklist). The reviewer-estimated LODs for the primary sludge samples ranged from 0.1 ng/mL for fenpropathrin to 16 ng/mL for permethrin and the LOQs ranged from 0.1 ng/mL for fenpropathrin to 22 ng/mL for permethrin. The reviewer estimates of the LODs for the dewatered cake samples were from 'unable to calculate' (due to being reported as non-detect for fenpropathrin) to 100 ng/g for permethrin and for the LOQs ranged from 'unable to calculate' to 117 ng/g for permethrin. These LODs and LOQs are based upon only two matrix control samples measured.

In contrast, the registrant-claimed values for the LODs and LOQs were set arbitrarily. The claimed LODs for the primary sludge samples were set to ⅓ of the LOQ and ranged from 0.83-8.3 ng/mL and the LOQ ranged from 2.5-25 ng/mL. Meanwhile, the registrant-claimed LODs for the dewatered cake samples were also set to ⅓ of the LOQ and ranged from 8.3-83 ng/g and the LOQ ranged from 25-250 ng/g.

METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

This method is considered unacceptable. It was validated by the same laboratory that developed the method and it is unknown whether the author of the method was also the Laboratory Director or whether he was involved in the available validation. An independent validation was not completed and only one set of performance data was submitted. The LOQs and LODs were determined arbitrarily. Samples were analyzed at the registrant-set LOQ (while some samples were tested at a multiple above the LOQ), and at 100 LOQ (it is recommended that the samples be tested at 10 LOQ). Furthermore, only three samples were tested at 100 LOQ (it is recommended that five samples be tested). Since it is not possible to obtain matrix control samples completely free of pesticides and because only two control matrix samples were tested, the reviewer-estimated LODs and LOQs are highly uncertain.

These deficiencies are considered major and the method provides only limited useful information and may not be upgraded by the submission of additional data. The registrant should provide a method with an independent laboratory validation. Furthermore, justification for the LOD and LOQ values and comparison to relevant or expected concentrations for the primary sludge samples should be provided. For the dewatered cake samples, the LOC and LOD values should be relevant relative to environmental concentration levels, and if possible, expected concentrations in surface waters after application of biosolids to land should be compared to endpoints such as those obtained from ecological effects studies (*i.e.*, LC_{50}s or NOAECs times their respective LOCs).

COMPLIANCE

Signed and dated Data Confidentiality and Quality Assurance statements were not provided. A signed Approvals page was provided (p. 2).

A. BACKGROUND INFORMATION

Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin are synthetic pyrethroid insecticides subject to EPA's

Registration Review (refer to http://www.epa.gov/oppsrrd1/reevaluation/pyrethroids-pyrethrins.html accessed 10/05/2011) and to CDPR's Reevaluation (refer to http://www.cdpr.ca.gov/docs/registration/reevaluation/chemicals/pyrethroids.htm accessed 10/05/2011). Pyrethroids may be used in multiple products both in agricultural and non-agricultural (*i.e.*, urban) settings. The primary biological effects of pyrethroids on insects and vertebrates reflect an inhibition of the correct firing of neurotransmitter deliver signals from one cell to another via nerve membrane inhibition of the voltage gated Ca^{2+} channels (calcium ion channels), coupled with a stimulatory effect on the voltage gated Na^{+} channels (sodium ion channels). Relative to physiological responses, researchers have designated two types of pyrethroids, Type I (*e.g.*, bifenthrin and permethrin) and Type II (*e.g.*, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin and *lambda*-cyhalothrin). Structurally, Type I pyrethroids lack the cyano-group that characterizes Type II pyrethroids.

TABLE A.1. Test Compound Nomenclature

Parameter	Value
Common name	Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin
Company experimental name	Not reported
IUPAC name	For chemical names, lot numbers, CAS #'s and structures see the Attachment II. Sources of test compounds, purities, lot numbers, expiration dates, and storage conditions are also shown in the Attachment II.
CAS Name	
CAS #	
Structure	

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound

Parameter	Value
Melting point/range (ºC)	These properties were not provided in the study report.
pH	
Density (g/cm^3)	
Water solubility at 20 ºC (mg/L)	
Solvent solubility at 20 ºC (mg/L)	
Vapor pressure at 20 or 25ºC (torr)	
Dissociation constant (pK_a)	
Octanol/water partition coefficient	
UV/visible absorption spectrum (nm)	

B. MATERIALS AND METHODS

B.1. Principle of Method

TABLE B.1. Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied	
Parameter	**Value**
Method ID	Meth-204 and Meth-205 using GC-MS NCI
Analytes	Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin
Extraction solvent/ technique	Methanol:water (1:1 v/v) (75 mL) and hexane (100 mL) are added to 50 mL samples of primary sludge or 5.00 g dewatered cake. Samples are shaken on a platform shaker for 1 hour. Then the mixture is centrifuged at ~2,500 rpm for a minimum of 10 minutes. The upper hexane layer is transferred to a 4 oz Qopak jar. One 1.0 oz aliquot is removed and processed via SPE cleanup.
Cleanup strategies	The 1.0 oz aliquot hexane sample is passed through a conditioned Varian Silica Bond Elut™ SPE cartridge, washed with 15 mL hexane, analytes eluted with 6 mL hexane: diethyl ether (9:1, v/v) into a test tube (13 x 100 mm). The eluate is evaporated to dryness under a stream of nitrogen using an N-Evap evaporator set to $\leq 40^0$C, redissolved in 2.5 mL of 0.1% peanut oil in acetone solution and sonicated.
Instrument/Detector	Agilent 6890 GC equipped with an Agilent 5973N mass selective detector (MS) operated in negative chemical ionization mode(NCI), GC inlet liner ; 4 mm i.d. gooseneck splitless liner packed with Carbo Frit™ (Restek), a HP 7683 autosampler, and a HP G1701CA MS ChemStation. Carrier gas helium injection volume 4 µL, column flow 0.9 mL/min constant flow, gradient temperature as specified in the document, ranging from 80 to 305^0C. A 30 m x 0.25 mm i.d. fused silica column cross-bonded with 0.25 µm film thickness Varian CP-Sil 8CB-MS. Gradient temperature ranging from 80^0 to 305^0C. An Agilent 5973N mass selective detector (MS) operated in negative chemical ionization mode (NCI).

C. RESULTS AND DISCUSSION

C.1. Recovery Results Summary

TABLE C.1.a. Recovery Results from Method Validation of Primary Sludge			
Analyte	**Spiking Levels (ng/mL)**	**Mean Recoveries Obtained (%)**	**Relative Standard Deviation**
Bifenthrin	5	80.5	1.2
Cyfluthrin	2.5	104	5.7
Cypermethrin	10	101	2.5
Deltamethrin	2.5	87.9	11
Esfenvalerate	2.5	99.7	5.7
Fenpropathrin	2.5	97.4	3.5

TABLE C.1.a. Recovery Results from Method Validation of Primary Sludge

Analyte	Spiking Levels (ng/mL)	Mean Recoveries Obtained (%)	Relative Standard Deviation
Lambda-cyhalothrin	2.5	103	4.0
Permethrin	25	92.8	4.0
Bifenthrin	250	78.5	1.3
Cyfluthrin	250	88.1	0.5
Cypermethrin	250	84.5	0.3
Deltamethrin	500	96.3	1.9
Esfenvalerate	250	89.6	0.7
Fenpropathrin	250	85.1	1.9
Lambda-cyhalothrin	250	92.4	0.7
Permethrin	2,500	81.6	0.9

TABLE C.1.b. Recovery Results from Method Validation of Dewatered Cake

Analyte	Spiking Levels (ng/g)	Mean Recoveries Obtained (%)	Relative Standard Deviation (%)
Bifenthrin	25	82.3	7.6
Cyfluthrin	25	106	2.7
Cypermethrin	50	93.2	6.7
Deltamethrin	50	86.6	11
Esfenvalerate	25	103	3.2
Fenpropathrin	25	96.4	4.2
Lambda-cyhalothrin	25	98.6	8.1
Permethrin	250	90.5	7.3
Bifenthrin	2,500	84.5	1.8
Cyfluthrin	2,500	92.5	2.3
Cypermethrin	2,500	89.0	2.8
Deltamethrin	5,000	99.2	2.6
Esfenvalerate	2,500	96.1	2.5
Fenpropathrin	2,500	89.0	1.8
Lambda-cyhalothrin	2,500	94.0	2.5
Permethrin	25,000	89.3	1.7

C.1.1. Method Characteristics

TABLE C.2. Method Characteristics			
Parameter	**Value**		
Analytes	Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin		
	Chemical\Sample	**Primary Sludge**	**Dewatered Cake**
Limit of Quantitation (**LOQ**)	Bifenthrin	1.6 ng/mL	17.8 ng/g
[Reviewer's rough estimate]	Cypermethrin	1.8 ng/mL	8.4 ng/g
	Cyfluthrin	1.0 ng/mL	2.8 ng/g
	Deltamethrin	0.1 ng/mL	ND in controls
	Esfenvalerate	0.8 ng/mL	9.9 ng/g
	Fenpropathrin	4.4 ng/mL	72.9 ng/g
	Lambda-cyhalothrin	5.0 ng/mL	41.1 ng/g
	Permethrin	21.8 ng/mL	117.1 ng/g
Limit of Detection (**LOD**)	Bifenthrin	1.4 ng/mL	14.9 ng/g
[Reviewer's rough estimate]	Cypermethrin	3.6 ng/mL	5.4 ng/g
	Cyfluthrin	0.9 ng/mL	31.7 ng/g
	Deltamethrin	0.5 ng/mL	2.7 ng/g
	Esfenvalerate	0.1 ng/mL	ND in controls
	Fenpropathrin	0.7 ng/mL	7.9 ng/g
	Lambda-cyhalothrin	2.0 ng/mL	30.9 ng/g
	Permethrin	16.4 ng/mL	100 ng/g
Accuracy/Precision at LOQ	At the LOQ average recoveries were within the range 78.5-106% and the relative standard deviations were within ND-11%.		
Reliability of the Method/[ILV]	Not applicable, no ILV conducted		
Linearity	For all analytes and according to reported data, $r^2 \geq 0.999$.		
Specificity	GC/MS – NCI appeared to be specific for the analytes based on inspection of the sample gas chromatographs. For six of the eight analytes there were 2 or 4 peaks. The response for the chemical was the sum total of all peaks. No peak confirmation or demonstration of specificity was performed.		
ND = Not Detected			

C.2. Independent Laboratory Validation (ILV)

No ILV was conducted.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

TABLE C.3.a. Recovery Results of the Method Obtained by an Independent Laboratory Validation for the Determination of Residues in Primary Sludge

Analyte	Spiking Level (units)	Mean Recoveries Obtained (%)	Relative Standard Deviation (%)
Bifenthrin	Not available, no true ILV was provided.		
Cypermethrin			
Cyfluthrin			
Deltamethrin			
Esfenvalerate			
Fenpropathrin			
Lambda-cyhalothrin			
Permethrin			

TABLE C.3.b. Recovery Results of the Method Obtained by an Independent Laboratory Validation for the Determination of Residues in Dewatered Cake

Analyte	Spiking Level (units)	Mean Recoveries Obtained (%)	Relative Standard Deviation (%)
Bifenthrin	Not available, no true ILV was provided.		
Cypermethrin			
Cyfluthrin			
Deltamethrin			
Esfenvalerate			
Fenpropathrin			
Lambda-cyhalothrin			
Permethrin			

D. CONCLUSION

The method was performed by the same laboratory that developed the method but an independent validation was not completed. The LOQs and LODs were determined arbitrarily. It is recommended that five samples be tested at the LOQ and at 10 LOQ. In this study, samples were analyzed at the LOQ (some samples were tested at a value above the LOQ due to interferences), and at 100 LOQ. Only three samples were tested at 100 LOQ. The registrant reported, "five instances where analyte residues found in the unfortified control samples were greater than 50% of the LOQ (in primary sludge: permethrin at an average of 14.0 ng/mL, cypermethrin at an average of 3.05 ng/mL and bifenthrin at an average of 1.35 ng/mL; and in dewatered cake: bifenthrin at an average of 13.6 ng/g and cypermethrin at an average of 27.6 ng/g)." Since it is not possible to obtain control matrix samples completely free of pesticides and because only two control matrix samples were tested, the reviewer-estimated LODs and LOQs are highly uncertain. No interferences were reported.

These deficiencies are considered major and the method provides only limited useful information and may not be upgraded by the submission of additional data. The registrant should provide a method with an independent laboratory validation, justify the LOD/ LOQ combination selected values and compare them to relevant environmental concentrations or to endpoints, such as those obtained from ecological effects studies (*e.g.*, LC_{50}s or NOAECs times their LOCs), particularly for the dewatered cake samples and the expected environmental concentrations in surface waters after application of biosolids to land.

There are two attachments to this review: Attachment I. Environmental Chemistry Method Review Checklist, and Attachment II. Names, chemical names, CAS numbers, structures, percent purities, lot numbers, sources and structures for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin.

MRID 48638601

Reviewer-Estimated LODs and LOQs for Primary Sludge and Dewatered Cake, from Two Matrix "Blank" Samples

					Est. LOD	Est. LOQ
ng/mL	Primary Sludge Matrix "Blank" (ng/mL)		Mean	SD	Mean + 3SD	Mean + 10 SD
Bifenthrin	1.33	1.37	1.35	0.028284	1.4	1.6
Cyfluthrin	0.625	0.445	0.535	0.127279	0.9	1.8
cypermethrin	3.19	2.91	3.05	0.19799	3.6	5.0
deltamethrin	1.2	0.714	0.957	0.343654	2.0	4.4
esfenvalerate	0.291	0.383	0.337	0.065054	0.5	1.0
fenpropathrin	0.0606	0.0587	0.05965	0.001344	0.1	0.1
lambda-cyhalothrin	0.666	0.688	0.677	0.015556	0.7	0.8
permethrin	14.6	13.5	14.05	0.777817	16.4	21.8

ng/g	Dewatered Cake Matrix "Blank" (ng/g)		Mean	SD	Mean + 3SD	Mean + 10 SD
Bifenthrin	13.3	13.9	13.6	0.424264	14.9	17.8
Cyfluthrin	4.35	3.73	4.04	0.438406	5.4	8.4
cypermethrin	28.6	26.7	27.65	1.343503	31.7	41.1
deltamethrin	17.2	8.73	12.965	5.989194	30.9	72.9
esfenvalerate	2.63	2.61	2.62	0.014142	2.7	2.8
fenpropathrin	ND	ND	ND	ND	ND	ND
lambda-cyhalothrin	6.87	7.27	7.07	0.282843	7.9	9.9
permethrin	91.4	94.8	93.1	2.404163	100.3	117.1

Data were obtained from Tables 1-2, pp. 32-35 of study report

Primary Sludge Sample-Results

MRID 48638601 Data were obtained from Table 1, pp. 32-33 of study report

Bolded value was considered outlier by the registrant as per Grubb's test; however, no further information was provided.

	Bifenthrin	Cyfluthrin	Cypermethrin	Deltamethrin	Esfenvalerate	Fenpropathrin	l-cyhalothrin	Permethrin
Primary Sludge Controls	1.35	0.535	3.05	0.957	0.337	0.05965	0.677	14.05
ng/mL found in primary sludge	5.38	3.92	12.8	4.87	2.65	2.38	3.20	36.6
	5.39	3.25	13.1	4.94	2.80	2.60	3.32	37.9
	5.32	2.94	13.1	6.12	2.83	2.46	3.09	37.5
	5.44	3.24	13.5	5.47	3.05	2.55	3.34	38.4
	5.34	3.07	13.1	5.37	2.82	2.48	3.29	35.8
ng/mL corrected for control	4.03	3.39	9.75	3.91	2.31	2.32	2.52	22.55
	4.04	2.72	10.05	3.98	2.46	2.54	2.64	23.85
	3.97	2.41	10.05	5.16	2.49	2.40	2.41	23.45
	4.09	2.71	10.45	4.51	2.71	2.49	2.66	24.35
	3.99	2.54	10.05	4.41	2.48	2.42	2.61	21.75
ng/mL fortification level	5.0	2.5	10	5.0	2.5	2.5	2.5	25
Percent recovered	81	**135**	98	78	93	93	101	90
	81	109	101	80	99	102	106	95
	79	96	101	103	100	96	97	94
	82	108	105	90	109	100	107	97
	80	101	101	88	99	97	105	87
Mean	80.5	103.6	100.7	87.9	99.7	97.4	102.8	92.8
Standard deviation	0.9	5.9	2.5	10	5.7	3.4	4.1	4.2
Relative standard deviation	1.2	5.7	2.5	11	5.7	3.5	4.0	4.5
Higher Fortification Level:								
ng/mL found in primary sludge	198	220	214	489	226	212	232	2039
	195	220	214	487	223	209	230	2048
	200	222	215	472	224	217	233	2074

ng/mL corrected for control	197	219	211	488	226	212	231	2025
	194	219	211	486	223	209	229	2034
	199	221	212	471	224	217	232	2060
ng/mL fortification level	250	250	250	500	250	250	250	2500
Percent recovered	79	88	84	98	90	85	93	81
	77	88	84	97	89	84	92	81
	79	89	85	94	89	87	93	82
Mean	78.5	88.1	84.5	96.3	89.6	85.1	92.4	81.6
Standard deviation	1.0	0.5	0.2	1.9	0.6	1.6	0.6	0.7
Relative standard deviation	1.3	0.5	0.3	1.9	0.7	1.9	0.7	0.9

Dewatered Cake Sample-Results

MRID 48638601

Data were obtained from Table 2, pp. 34-35 of study report

	Bifenthrin	Cyfluthrin	Cypermethrin	Deltamethrin	Esfenvalerate	Fenpropathrin	l-cyhalothrin	Permethrin
Dewatered Cake Controls	13.6	4.04	27.65	12.965	2.62	0	7.07	93.1
ng/g found in dewatered cake	33.0	29.6	68.7	52.1	27.5	22.7	28.7	304
	32.8	30.4	75.0	52.0	27.8	23.5	31.3	303
	34.0	30.3	76.1	55.1	29.2	25.2	32.0	321
	34.4	31.4	75.4	60.2	28.2	24.9	34.2	342
	36.7	31.2	76.0	61.8	29.3	24.2	32.4	327
ng/g corrected for control	19.4	25.6	41.1	39.1	24.9	22.7	21.6	211
	19.2	26.4	47.4	39.0	25.2	23.5	24.2	210
	20.4	26.3	48.5	42.1	26.6	25.2	24.9	228
	20.8	27.4	47.8	47.2	25.6	24.9	27.1	249
	23.1	27.2	48.4	48.8	26.7	24.2	25.3	234
ng/g fortification level	25	25	50	50	25	25	25	250
Percent recovered	78	102	82	78	100	91	87	84
	77	105	95	78	101	94	97	84
	82	105	97	84	106	101	100	91
	83	109	96	94	102	100	109	100
	92	109	97	98	107	97	101	94
Mean	82.3	106.2	93.2	86.6	103.1	96.4	98.6	90.5
Standard deviation	6.2	2.9	6.3	9.1	3.3	4.1	8.0	6.6
Relative standard deviation	7.6	2.7	6.7	11	3.2	4.2	8.1	7.3
Higher Fortification Level:								
ng/g found in dewatered cake	2137	2318	2251	4838	2390	2207	2327	22690
	2157	2370	2317	5100	2470	2271	2425	22593
	2082	2263	2192	4979	2354	2199	2322	21998

ng/g corrected for control	2123	2314	2223	4825	2387	2207	2320	22597
	2143	2366	2289	5087	2467	2271	2418	22500
	2068	2259	2164	4966	2351	2199	2315	21905
ng/g fortification level	2500	2500	2500	5000	2500	2500	2500	25000
Percent recovered	85	93	89	97	95	88	93	90
	86	95	92	102	99	91	97	90
	83	90	87	99	94	88	93	88
Mean	84.5	92.5	89.0	99.2	96.1	89.0	94.0	89.3
Standard deviation	1.6	2.1	2.5	2.6	2.4	1.6	2.3	1.5
Relative standard deviation	1.8	2.3	2.8	2.6	2.5	1.8	2.5	1.7

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

Attachment I:

ENVIRONMENTAL CHEMISTRY METHOD (ECM) STANDARD EVALUATION PROCEDURE (SEP) CHECKLIST: BACKGROUND AND INITIAL REVIEW INFORMATION

"Validation of the Residue Analytical Methods: 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin and Permethrin in **Wastewater Treatment Primary Sludge**,' Dated October 21, 2010 and 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin and Permethrin in **Wastewater Treatment Dewatered Cake**,' Dated October 20, 2010." (MRID 48638601)

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

I. Background Information

A.	**Title of Method**	"Validation of the Residue Analytical Methods: 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin and Permethrin in Wastewater Treatment Primary Sludge,' Dated October 21, 2010 and 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin and Permethrin in Wastewater Treatment Dewatered Cake,' Dated October 20, 2010." Laboratory Validation of Morse Laboratories, LLC Analytical Methods Meth-204 and Meth-205. Morse Labs Project No.: ML10-1641-HQI. Date of the Report February 3, 2011. Performed by Morse Laboratories, LLC, and Submitted by Pyrethroid Working Group (c/o Daniel M. Tessier, Ph.D.). Author: J.M. Willoh
B.	**ECM No.** [For BEAD]	
C.	**MRID No.**	48638601
D.	**Matrix**	Wastewater treatment primary sludge and dewatered cake
E.	**Analytes detected**	All analytes are parent synthetic pyrethroid insecticides: bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin. For structures, CAS Reg. No., CAS names, IUPAC names and structures, refer to the Attachment II.

II. Information about the Laboratory

A.	**Name**	Morse Laboratories, LLC
B.	**Address**	1525 Fulton Avenue Sacramento, CA 95825
C.	**Telephone No.**	Not provided
D.	**Name of the Study Director**	Jeri M. Willoh, Analytical Project Coordinator
E.	**Name of the Lead Chemist**	Seth Nasca, Associate Chemist
F.	**Laboratory Validation:**	Kevin Clark, Method Author

III. Method Summary Information for Analytes:

"The purpose of this study was to validate these methods according to the requirements of the Pyrethroid Working Group. The validations were performed on wastewater treatment samples of primary sludge and dewatered cake collected from a publicly owned treatment works (POTW) in Suffern, New York, a secondary treatment facility." "The primary sludge samples were collected from the primary settling tanks. The samples are a combination of primary settled solids after pretreatment (grit removal, bar

screens) as well as waste solids after activated sludge biological treatment. The solids are co-thickened in the primary settling tanks before being transferred to the anaerobic digesters. The dewatered cake was collected as digested sludge from the anaerobic digesters and was dewatered using a centrifuge."

A.	**Statement of Data Confidentiality**	No. The method does not provide a statement regarding data confidentiality. This method was submitted to CDPR under California Notice 2006-13.
1.	**Is the Method Classified or Confidential?**	No statement claiming confidentiality was provided.
2.	**Submitted Prior to 2008 with a Non-Standard Claim of Confidentiality?**	No.
B.	**Sample Preparation**	"Upon receipt of the samples at the laboratory, they were immediately placed in refrigerated storage (typically 1-8 °C), where they remained pending sub sampling and analysis." No further sample preparation was required.
C.	**Sample Extraction**	Methanol:water (1:1 v/v) (75 mL) and hexane (100 mL) are added to 50 mL samples of primary sludge or 5.0 g dewatered cake. Samples are shaken on a platform shaker for 1 hour (100-150 cpm). Then the mixture is centrifuged at ~2,500 rpm for a minimum of 10 minutes. The upper hexane layer is transferred to a 4 oz Qopak jar. One 1.0 oz aliquot is removed and processed via SPE cleanup.
D.	**Sample Cleanup**	The 1.0 oz aliquot hexane sample is passed through a conditioned Varian Silica Bond Elut™ SPE cartridge, washed with 15 mL hexane, analytes eluted with 6 mL hexane: diethyl ether (9:1, v/v) into a test tube (13 x 100 mm). The eluate is evaporated to dryness under a stream of nitrogen using an N-Evap evaporator set to $\leq 40^0$C, redissolved in 2.5 mL of 0.1% peanut oil in acetone solution and sonicated.
E.	**Sample Derivatization**	Not applicable to this procedure.
F.	**Sample Analysis**	Residues determined using GC-MS/NCI
1.	**Instrumentation**	Agilent 6890 GC equipped with an Agilent 5973N mass selective detector (MS) operated in negative chemical ionization mode(NCI), GC inlet liner ; 4 mm i.d. gooseneck splitless liner packed with Carbo Frit™ (Restek), a HP 7683 autosampler, and a HP G1701CA MS ChemStation. Carrier gas helium injection volume 4 µL, column flow 0.9 mL/min constant flow, gradient temperature as specified in the document, ranging from 80 to 305^{0}C.
2.	**Primary Column**	30 m x 0.25 mm i.d. fused silica column cross-bonded with 0.25 µm film thickness Varian CP-Sil 8CB-MS.
3.	**Confirmatory Column**	MS considered a confirmatory technique.
4.	**Detector**	Agilent 5973N mass selective detector (MS) operated in negative chemical ionization mode (NCI).

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

5.	**Other Confirmatory Techniques**	Target ions and qualifier ions, and retention times as shown in the document.
6.	**Other Relevant Information**	All the analytes except for bifenthrin and fenpropathrin show more than one peak in GC. When making calculations, this was considered by calculating the total peak response (total of all isomer responses/chemical).

G.	**Detection and Quantitation Limits**			
1.	**Limit of Quantitation (LOQ)**	***Reviewer-estimated based on only two matrix "blanks"**		
	Primary Sludge Samples	**Claimed in Method**	**Estimated***	
	Bifenthrin	2.5 ng/mL	1.6 ng/mL	
	Cyfluthrin	2.5 ng/mL	1.8 ng/mL	
	Esfenvalerate	2.5 ng/mL	1.0 ng/mL	
	Fenpropathrin	2.5 ng/mL	0.1 ng/mL	
	Lambda-cyhalothrin	2.5 ng/mL	0.8 ng/mL	
	Deltamethrin	5.0 ng/mL	4.4 ng/mL	
	Cypermethrin	2.5 ng/mL	5.0 ng/mL	
	Permethrin	25 ng/mL	22 ng/mL	
	Dewatered Cake Samples	**Claimed in Method**	**Estimated***	
	Bifenthrin	25 ng/g	18 ng/g	
	Cyfluthrin	25 ng/g	8.4 ng/g	
	Esfenvalerate	25 ng/g	2.8 ng/g	
	Fenpropathrin	25 ng/g	Reported not detected in control smpls	
	Lambda-cyhalothrin	25 ng/g	9.9 ng/g	
	Deltamethrin	50 ng/g	73 ng/g	
	Cypermethrin	25 ng/g	41 ng/g	
	Permethrin	250 ng/g	117 ng/g	
2.	**Limit of Detection (LOD)**	***Reviewer-estimated based on only two matrix "blanks"**		
	Primary Sludge Samples	**Claimed (⅓ LOQ)**	**Estimated***	
	Bifenthrin	0.83 ng/mL	1.4 ng/mL	
	Cyfluthrin	0.83 ng/mL	3.6 ng/mL	
	Cypermethrin	0.83 ng/mL	0.9 ng/mL	
	Esfenvalerate	0.83 ng/mL	0.5 ng/mL	
	Fenpropathrin	0.83 ng/mL	0.1 ng/mL	
	Lambda-cyhalothrin	1.7 ng/mL	0.7 ng/mL	
	Deltamethrin	0.83 ng/mL	2.0 ng/mL	
	Permethrin	8.3 ng/mL	16 ng/mL	
	Dewatered Cake Samples	**Claimed (⅓ LOQ)**	**Estimated***	
	Bifenthrin	8.3 ng/g	15 ng/g	

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

	Cyfluthrin	8.3 ng/g	5.4 ng/g	
	Cypermethrin	8.3 ng/g	32 ng/g	
	Esfenvalerate	8.3 ng/g	2.7 ng/g	
	Fenpropathrin	8.3 ng/g	Reported not detected in control smpls	
	Lambda-cyhalothrin	17 ng/g	7.9 ng/g	
	Deltamethrin	8.3 ng/g	31 ng/g	
	Permethrin	83 ng/g	100 ng/g	

H. Recovery (Accuracy) /Precision Data

Primary Sludge Samples

	At LOQ (%) [1]				At 100 LOQ (%) [1]			
	Range	Mean	SD	RSD	Range	Mean	SD	RSD
Bifenthrin	79-82[2]	80.5	0.9	1.2	77-79	78.5	1.0	1.3
Cyfluthrin	96-109[3]	104	5.9	5.7	88-89	88.1	0.5	0.5
Cypermethrin	98-105[4]	101	2.5	2.5	84-85	84.5	0.2	0.3
Deltamethrin	78-103[2]	87.9	10	11	94-98	96.3	1.9	1.9
Esfenvalerate	93-109	99.7	5.7	5.7	89-90	89.6	0.6	0.7
Fenpropathrin	93-102	97.4	3.4	3.5	84-87	85.1	1.6	1.9
Lambda-cyhalothrin	97-106	103	4.1	4.0	92-93	92.4	0.6	0.7
Permethrin	87-97	92.8	4.2	4.0	81-82	81.6	0.7	0.9

1. **These recoveries are based upon an arbitrary LOQ that was set by the registrant. At the LOQ, five samples were tested while at 100 LOQ only three samples were tested. No samples were tested at 10 LOQ.** 2. Sample was actually tested at 2 x LOQ instead of LOQ. 3. One outlier at 135% was determined per Grubbs' test; no further information was provided. 4. Sample was actually tested at 4 x LOQ instead of LOQ.

Dewatered Cake Samples

	At LOQ (%)				At 100 LOQ (%)			
	Range	Mean	SD	RSD	Range	Mean	SD	RSD
Bifenthrin	77-92	82.3	6.2	7.6	83-86	84.5	1.6	1.8
Cyfluthrin	102-109	106	2.9	2.7	90-95	92.5	2.1	2.3
Cypermethrin	82-97[2]	93.2	6.3	6.7	87-92	89.0	2.5	2.8
Deltamethrin	78-94[2]	86.6	9.1	11	97-102	99.2	2.6	2.6
Esfenvalerate	100-107	103	3.3	3.2	94-99	96.1	2.4	2.5
Fenpropathrin	91-101	96.4	4.1	4.2	88-91	89.0	1.6	1.8
Lambda-cyhalothrin	87-109	98.6	8.0	8.1	93-97	94.0	2.3	2.5
Permethrin	84-100	90.5	6.6	7.3	88-90	89.3	1.5	1.7

1. **These recoveries are based upon an arbitrary LOQ that was set by the registrant. At the LOQ, five samples were tested while at 100 LOQ only three samples were tested. No samples were tested at 10 LOQ.** 2. Sample was actually tested at 2 x LOQ instead of LOQ.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

IV. Detailed Information about the Method

		YES	NO	REVIEW FURTHER
A.	**Does the method require spiking with the analytes of interest?**		X	
B.	**If the method requires explosive or carcinogenic reagents, are proper precautions explained?**	_Not applicable		
C.	**Is the following information supplied?**			
1.	**Detailed stepwise description of:**			
a.	**The sample preparation procedure?**	X		
b.	**The sample spiking procedure?**	X		
c.	**The extraction procedure?**	X		
d.	**The derivatization procedure?**	_Not applicable		
e.	**The clean-up procedure?**	X		
f.	**The analysis procedure?**	X		
2.	**Procedures for:**			
a.	**Preparation of standards?**	X		
b.	**Calibration of instrument?**	X		
3.	**List of glassware and chemicals**	X		
a.	**Are sources recommended?**		X	
b.	**Are they commercially available?**	X		
4.	**Name, model, *etc.*, of the instrument, column, detector, *etc.*, used?**	X		
a.	**Are sources recommended?**	X		
b.	**Are they commercially available?**	X		
5.	**LOD**			
a.	**Is there an explanation of how it was calculated?**		X	
b.	**Is it a scientifically accepted procedure?**		X	

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
c.	Is the matrix blank free of interferences(s) at the retention time, wavelength, *etc.*, of the analyte(s) of interest?		X	
6.	LOQ			
a.	Is there an explanation of how it was calculated?		X	
b.	Is it a scientifically accepted procedure?		X	
7.	Precision and accuracy data			
a.	Were there an adequate number of spiked samples analyzed?		X	
b.	Are the mean recoveries between 70-120%?	X		
c.	Are the RSDs of the replicates 20% or less at or above the LOQ?	X		
8.	Description and/or explanation of:			
a.	Areas where problems may be encountered?			X
b.	Steps that are critical?			X
c.	Interferences that may be encountered?		X	
9.	Characterization of the Matrices?		X	

V. Representative Chromatograms

		YES	NO	REVIEW FURTHER
A.	Are there representative chromatograms for:			
1.	Analytes in each matrix at the LOQ and 10 x LOQ?		X	
2.	Method blanks?	X		
3.	Matrix blanks?	X		
4.	Standard curves?	X		

a.	**Do the standard curves have acceptable linearity?**	X		
5.	**Standards that can be used to recalculate some of the values for analyte(s) in the sample chromatograms?**			X
B.	**Can the responses of the analytes in the chromatograms of the lowest spiking level be accurately measured?**	X		

VI. Good Laboratory Practice (GLP) Standards

		YES	NO	REVIEW FURTHER
A.	**Is there a statement of adherence to the FIFRA GLP standards?**		X	

VII. Independent Lab Validation (ILV)

		YES	NO	REVIEW FURTHER
A.	**Was an ILV performed?**		X	
B.	**Was the validation independent?**	Not applicable, ILV not performed.		
C.	**Did the ILV's precision/accuracy data meet the criteria established in OPPTS Guideline 850.6100?**	Not applicable, ILV not performed.		
D.	**Were recommendations of major or minor modifications to the method made by the independent lab performing the ILV? If major modifications were suggested, what were they?**	Not applicable, ILV not performed.		

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

VIII. Completeness

		YES	NO	REVIEW FURTHER
A.	**Has enough information been supplied to do a proper review?**		X	
B.	**Has enough information been supplied to do a laboratory evaluation, if requested?** [BEAD's ECB determination.]			
C.	**Are all steps in the method scientifically sound?**	X		
D.	**Is a confirmatory method or technique provided?**	X		
E.	**Check the category below which best describes this ECM.**	**Satisfactory**	**Major Deficiencies**	**Minor Deficiencies**
1.			X	

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

IX. Recommendations

The analytical method was validated by the same laboratory that developed the method. The LOQs and LODs were determined arbitrarily. Samples were analyzed at the LOQ (some samples were actually tested at above the LOQ), and 100 LOQ; however, it is recommended to test at LOQ and at 10 LOQ. Furthermore, only three samples were tested at 100 LOQ (recommended five samples). Since it is not possible to obtain control matrix samples completely free of pesticides and because only two control matrix samples were tested, the estimated LODs and LOQs are highly uncertain. Registrant-reported LODs and LOQs appeared inappropriate, when compared to the reviewer-estimated values.

These deficiencies are considered major and the method provides only limited useful information and may not be upgraded by the submission of additional data. The registrant should provide a method with an independent laboratory validation, justify the LOD and LOQ combination selected values, and compare them to relevant endpoints, such as those obtained from ecological effects studies (*e.g.*, LC_{50}s and NOAECs), particularly for the dewatered cake samples, and expected concentrations in surface waters after land application of biosolids.

José Luis Meléndez 10/24/2011

Primary Reviewer: José L. Meléndez, Chemist

11/01/2011

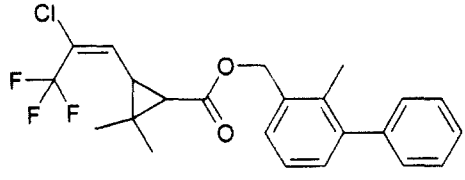
Secondary Reviewer: Reuben Baris, Environmental Scientist
EFED's Pyrethroid Review Team Representative

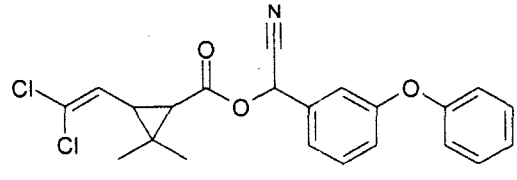
Attachment II:

Names, chemical names, CAS numbers, structures, percent purities, lot numbers, sources and structures for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin[1]

[1] Structures were taken from the ECM for influent/effluent that was concurrently reviewed.

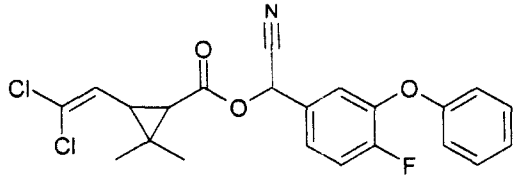
ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

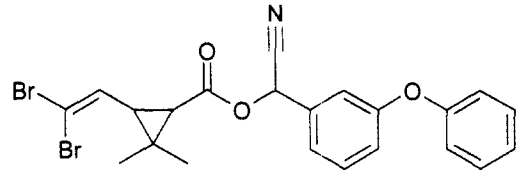
Compound	Bifenthrin
IUPAC Name:	2-methylbiphenyl-3-ylmethyl (*Z*)-(1*RS*,3*RS*)-3-(2-chloro-3-3-3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	82657-04-3
CAS Name:	(2-methyl[1,1'-biphenyl]-3-(2-chloro-3-3-3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	97.8
Lot No.:	BI-29
Source:	FMC Agricultural Products
Expiration Date:	8/2012
Storage:	Typically -8 °C to -22 °C

Compound	Cypermethrin
IUPAC Name:	(*RS*)-α-cyano-3-phenoxybenxyl (1*RS*,3*RS*;1*RS*,3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	52315-07-8
CAS Name:	Cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	99.3
Lot No.:	479549
Source:	Syngenta Crop Protection
Expiration Date:	8/31/2011
Storage:	Typically 1 °C to 8 °C

t/E

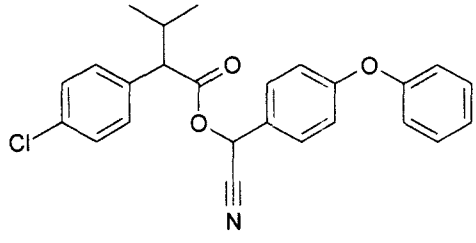
ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

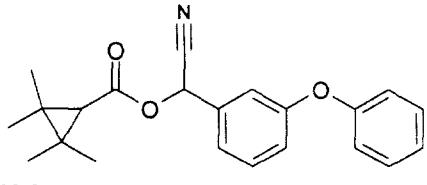
Compound	Cyfluthrin
IUPAC Name:	*(RS)*-α-cyano-4-fluoro-3-phenoxybenzyl (1*RS*,3*RS*;1*RS*,3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	68359-37-5
CAS Name:	Cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	98
Lot No.:	446-18A
Source:	Chem Service
Expiration Date:	04/2014
Storage:	Typically -8 °C to -22 °C

Compound	Deltamethrin
IUPAC Name:	(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	52918-63-5
CAS Name:	1-[*R*-[1-α(*S**),3α]]-cyano(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	99.5
Lot No.:	437-93B
Source:	Chem Service
Expiration Date:	02/2013
Storage:	Typically -8 °C to -22 °C

I/E

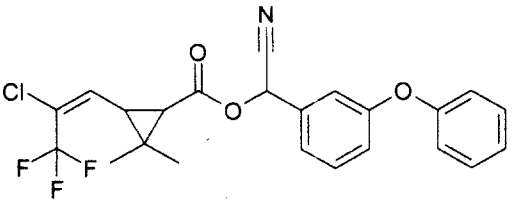
ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

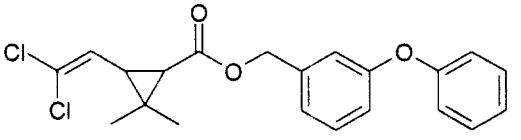
Compound	Esfenvalerate
IUPAC Name:	(*S*)-α-cyano-3-phenoxybenzyl (*S*)-2-(4-chlorophenyl)-3-methylbutyrate
CAS Number:	66230-04-4
CAS Name:	[*S*-(*R**,*R**)]-cyano(3-phenoxyphenyl)methyl 4-chloro-2-(1-methylethyl)benzeneacetate
Structure:	
% Purity:	98.7
Lot No.:	419-137B
Source:	Chem Service
Expiration Date:	03/2015
Storage:	Ambient

Compound	Fenpropathrin
IUPAC Name:	(*RS*)-α-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate
CAS Number:	64257-84-7
CAS Name:	Cyano(3-phenoxyphenyl)methyl 2,2,3,3-tetramethylcyclopropanecarboxylate
Structure:	
% Purity:	99.5
Lot No.:	414-115A
Source:	Chem Service
Expiration Date:	12/2013
Storage:	Typically -8 °C to -22 °C

I/E

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

Compound	Lambda-cyhalothrin
IUPAC Name:	A reaction product containing equal quantities of (*S*)-α-cyano-3-phenoxybenzyl (*Z*)-(1*R*,3*R*)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate and (*R*)-α-cyano-3-phenoxybenzyl (*Z*)-(1*R*,3*R*)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	91465-08-6
CAS Name:	[1α(*S**),3α(*Z*)]-(±)-cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	99.5
Lot No.:	446-94A
Source:	Chem Service
Expiration Date:	5/2014
Storage:	Typically 1 °C to 8 °C

Compound	Permethrin
IUPAC Name:	3-phenoxybenzyl (1*RS*,3*RS*;1*RS*,3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	52645-53-1
CAS Name:	(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	98.0
Lot No.:	401-113A
Source:	Chem Service
Expiration Date:	04/2011
Storage:	Typically 1 °C to 8 °C

I/E

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

MEMORANDUM

DATE: November 9, 2011

SUBJECT: EFED Comments on the Pyrethroid Working Group's Environmental Chemistry Methods for Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin for the Analysis of Influent and Effluent (*i.e.*, Wastewaters), Primary Sludge and Dewatered Cake (*i.e.*, Biosolid) Samples from Publicly Owned Treatment Works
PC Codes: 128825, 109702, 128831, 097805, 109303, 127901, 128897, 109701
DP Barcode: D395988

FROM: José L. Meléndez, Chemist, ERB5
and: Pyrethroid Review Team
Environmental Fate and Effects Division (7507P)

THROUGH: Mah T. Shamim, Ph.D., Branch Chief ERB5
Pyrethroid Review Team Lead
Environmental Fate and Effects Division (7507P)

TO: Monica Wait, Chemical Review Manager
Michael Goodis, Branch Chief
Risk Management and Implementation Branch III
Pesticide Re-Evaluation Division (7508P)

The Environmental Fate & Effects Division (EFED) has reviewed two studies submitted by the Pyrethroid Working Group. The EFED evaluated all the information available and a summary of the findings is presented in **Table 1**. For details about the studies refer to the attached Data Evaluation Records (DERs).

Table 1. Environmental Fate Data Requirements for Eight Pyrethroids

Guideline Number	Data Requirement	Bibliographic Citation	Study classification
Non-guideline	Environmental Chemistry Method	48638501	Unacceptable
Non-guideline	Environmental Chemistry Method	48638601	Unacceptable

Citations for these studies are as follows:

- Willoh, J.M., 2010, "Validation of Morse Laboratories, LLC Analytical Method (METH-201): "Determination of residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater (Influent and Effluent)," Dated September 30, 2010. Morse Labs Project No.: ML10-1602-PWG. Date of the Report December 3, 2010. Unpublished study performed by Morse Laboratories, LLC, and submitted by the Pyrethroid Working Group (PWG), 200 pp. (MRID 48638501); and,

- Willoh, J.M., 2010, "Validation of the Residue Analytical Methods: 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater Treatment Primary Sludge,' Dated October 21, 2010 and 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater Treatment Dewatered Cake,' Dated October 20, 2010." Laboratory Validation of Morse Laboratories, LLC Analytical Methods Meth-204 and Meth-205. Morse Labs Project No.: ML10-1641-HQI. Date of the Report February 3, 2011. Unpublished study performed by Morse Laboratories, LLC, and submitted by the Pyrethroid Working Group, 219 pp. (MRID 48638601).

The first method referenced above is designed for the analysis of influent and effluent wastewaters from Publicly Owned Treatment Works (POTWs) while the second method is for the analysis of primary sludge and dewatered cake (*i.e.*, biosolids) from POTWs. Samples were taken from a POTW in Suffern, NY. These documents were initially submitted to the California Department of Pesticide Regulation (CDPR) as part of its directive in a letter from Ann M. Prichard, Chief of Pesticide Registration Branch, to the registrants, dated 07/15/2011. In the letter, CDPR requested "[a]cceptable analytical methods for POTW influent, effluent, and biosolids for the following eight pyrethroids: bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin, and permethrin." The Agency reviewed the studies following current "Guidance for Processing and Reviewing Environmental Chemistry Methods," dated 02/24/2011. EFED is providing the following general comments on the referenced methods.

The EPA found that these environmental chemistry methods (ECMs) do not meet the criteria for scientifically valid methods for the following main reasons:

1. According to EFED's Standard Evaluation Procedure (SEP), "Reviewing Environmental Chemistry Methods," dated 12/01/2010 and approved 02/22/2011, an initial screen of the methods was performed. EFED found during the screen that the studies were not reviewable because independent laboratory validation reports (ILVs) for the ECMs were not available. Furthermore, two complete sets of performance data were not provided for each ECM. In addition, at least five spiked samples were not analyzed at the LOQ and at 10 x LOQ. A minimum of five spiked samples should be analyzed at each concentration (*i.e.*, the LOQ and 10 x LOQ). Even though these studies were not reviewable, at CDPR's request EFED completed the review of the ECMs.
2. The LOQs and LODs were determined arbitrarily. Detection limits should not be based on arbitrarily selected lowest concentration in the spiked samples. 40 CFR Part 136, Appendix B lists some scientifically accepted procedures for estimating detection limits.

LODs are often calculated as the mean matrix blank value plus 3 times the standard deviation; LOQs are often calculated as the mean matrix blank value plus 10 times the standard deviation.

3. Since it is not possible to obtain matrix blank samples completely free of pyrethroid pesticides and because only two matrix control samples were tested, the reviewer-estimated LODs and LOQs are highly uncertain.
4. A signed and dated Data Confidentiality and Quality Assurance statements were not provided.
5. For some of the chemicals, samples were not tested at the selected LOQ. Instead, they were tested at a multiple value (*e.g.*, 2 x LOQ or 4 x LOQ), due to interferences in matrix blanks samples. Conversely, for some the chemicals, the results were reported as "not detected" in the matrix blank precluding LOD and LOQ estimation.
6. Some samples were regarded as outliers; however, no supporting statistical information was provided. It was only stated that they were outliers per Grubbs' test.

These deficiencies are considered major and the methods provide only limited useful information. The studies cannot be upgraded by the submission of additional data. The registrant should provide chemistry methods (ECMs) with independent laboratory validations (ILVs); in addition, justification for the LODs and LOQs selected should be provided. The LODs and LOQs should be compared to relevant expected concentrations for influent, effluent, primary sludge and biosolid samples, and to relevant ecological effects endpoints (*e.g.*, LC_{50}s or NOAECs times the levels of concern) for applicable samples.